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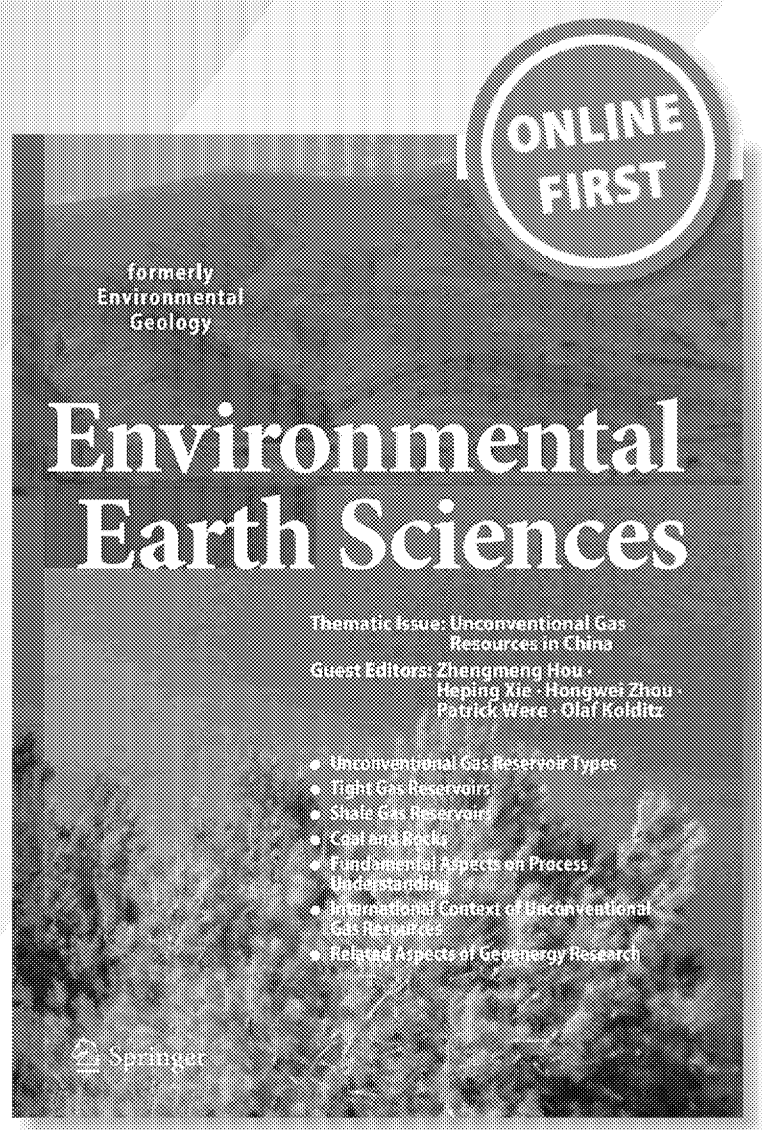

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ORIGINAL ARTICLE

Chemical composition of bottom sediments within black hills region reservoirs of South Dakota and Wyoming

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Abstract The objectives of this study were to determine the effect of heavy metals transported from mining areas due to historical mining activities within the Black Hills region of South Dakota and Wyoming US, and to evaluate the presence of major and trace elements resulting from influence of provenance, weathering, erosion, and sediment sorting within reservoir sediments. Soil core samples were collected from both inflow and outflow of the reservoirs. X-ray florescence analyses were performed to determine the presence of major and the trace elements concentration. Pactola and Sheridan Lakes had the highest concentration of As, Fe, Mn, and Rb/Sr ratios, while the Belle Fourche Reservoir had the highest U concentration. Spatial and temporal patterns of Rb/Sr ratio of the reservoir sediments were used to determine the weathering intensity of the catchment areas. With the exception of Angostura and LAK reservoirs, all Black Hills reservoirs were dominated by physical weathering processes within their respected watersheds. Immobile high field strength elements from within the reservoir sediments were higher compared to upper continental crust (UCC) concentrations, and further suggest the dominance of physical weathering processes for all reservoirs except LAK. Spider diagrams normalized to UCC concentrations indicate that Black Hills regional reservoirs were elevated in Zr, Hf, and U, further supporting the dominance of physical or mechanical weathering influences from their watersheds. Watersheds dominated by physical weathering processes are commonly subjected to high erosion, anthropogenic activities, and/or high precipitation processes.

Keywords Geochemistry · Reservoir sediment · Uranium · Mineralogy · Weathering

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Introduction

Mining-related activities in the Black Hills region of South Dakota (SD) and Wyoming (WY) US began with the European settlement in the region in the late 1800s. Black Hills region is the only region in SD which provides the geophysical setting for the precious mineral deposits. The past mining activities in the Black Hills can be divided into three groups: the northern hills with primarily gold mines, the central hills with pegmatite and gold mines, and the southern hills near Edgemont with U mining (Webb et al. 1998). Gold was discovered in 1874, and initial mining activity was limited to the placer mining in Custer, SD (Webb et al. 1998), followed by silver (Ag), base metals, pegmatite, oil and gas, sand and gravel, gypsum, and molybdenum (Mo). Most of these placer deposits were Proterozoic to Quaternary age (DeWitt et al. 1989). Hardrock mining of ore formations began in 1876, after the discovery of gold-bearing deposits. DeWitt et al. (1989) classified 1084 mines in 85 metallic mineral district in the Black Hills. The Homestake mine in Lead, SD was the largest gold producing mine in North America before it closed down in 2002. Uranium (U) mining also has a long history in the southern Black Hills region starting in 1951 (Page and Redden 1952). Nearly 1 million tons of U_3O_8

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were mined during the following 13 years, commonly without erosion controls or reclamation pursuant to mining laws of that time (e.g., Act of 1872 and 30 USC 541, 1955). As a result, there has been extensive environmental degradation from these mining and post-mining operations.

Environmental hazards associated with mining in the Black Hills includes acid mine drainage (AMD) and arsenic contamination in the northern Black Hills, and contamination associated with abandoned U mines and tailings in the southern Black Hills. There have been several investigative studies conducted on AMD and As contamination in the northern Black Hills. A report by Ecology Environment LLC (2004) concluded that the concentration of As, Be, Ca, Ag, Mn, Hg, and Se in the soil and sediment samples collected from the Gold Mountain mine site was 3 times background, with the highest concentration of As in soil and sediment samples were 159 and 787 mg/kg, respectively. Gold mining in the northern Black Hills region of SD has been a continual source of mining tailings discharge into the Whitewood Creek and transported into the Belle Fourche (BF) River and thence to the Cheyenne River. Horowitz et al. (1988) concluded that the high concentration of As in core sediments was likely transported from the banks or floodplains of Whitewood Creek and the BF River.

There is limited knowledge regarding the status, size, and locations of historical U mines at the Black Hills region. The U mining district north of Edgemont SD (Fall River County) has been well documented (Hall 1982; Davis et al. 1999; Rahn et al. 1996; Webb et al. 1998) with 24 abandoned U mines documented within the Edgemont district. Rahn et al. (1996) reported that dissolved uranium was detected at 2.6 ppm in water samples collected from standing water in several mines from the Edgemont district, while Davis et al. (1999) evaluated water-quality impacts from abandoned mines within the Bear Butte Creek basin of the northern Black Hill, and the headwaters of the Driftwood Creek basin within the uranium mining district of the southern Black Hills. They reported that water-quality impacts were limited to the Strawberry Creek and the Bear Butte Creek, while for Driftwood Creek, surface water-quality impacts were limited to a stock pond own-gradient from abandoned U mines. Webb et al. (1995) reported that mine pit waters contained 2 mg/L U within this same region (Rahn et al. 1996).

The accumulation of heavy metals and radionuclides within reservoir bottom sediments has been used to better understand historical pollution trends from mining-impacted watersheds (Rauch et al. 2006; Spliethoff and Hemond 1995). Factors known to influence metal transport to sediments include climate, chemical and physical properties of host materials, weathering processes, sediment transport energy, and anthropogenic activities (Das and Haake 2003; Reynolds et al. 2010). Reservoir bottom sediment profiles can provide a comprehensive understanding of source material transport phenomena and chronology for understanding the history of the environmental impacts incurred. The objective of this research was to determine the watershed impacts due to soil and water erosion from abandoned mining sites on and adjacent to US Forest Service (USFS) administered lands within the Black Hills region using major and trace element geochemistry signatures, and comparing those to known physical and chemical transport process signatures to elucidate potential transport processes within the potentially mining-impacted watersheds.

Geology and climate

The Black Hills region has a unique geological record. The oldest rocks in the Black Hills are Precambrian of metamorphic and igneous origin, found in the central hills of the eroded dome, and are the only exposed Precambrian rocks of Trans-Hudeon orogeny in the northern US (Roddy et al. 1991). The central part of the Black Hills is encircled by the younger Cambrian Deadwood Formation and the Jurassic Morrison Formation. Mineral deposits are limited to Precambrian rocks in the northern and central Black Hills and tertiary intrusions in the northern Black Hills (Webb et al. 1998). The metamorphic rocks of Precambrian age are mostly slates and quartzite. Rich (1981) divided Precambrian rocks of Black Hills into Archean, Oldest Early Proterozoic, Older Early Proterozoic, and Younger Early Proterozoic units. Archean metasedimentary rocks and Oldest Early Proterozoic rocks have limited exposures in the Little Elk Creek area and at Bear Mountain and Nemo area, respectively. Older Early Proterozoic unit chiefly contain conglomerate and quartzite. The source of these rocks is mainly Oldest Early Proterozoic unit, but Estes Formation with abundant feldspar and quartz clasts indicate Little Elk Granite source of Late Archean. Estes Formation in Nemo area consists of arkose, quartzite, and pelite. Nemo area also consists of dolomite and silty pelite of carbonate origin. Carbonate rocks at the west Nemo overlain by theoleiitic pillow basalt and maffic tuff and shale. Theoleiitic basalt without pillow structure is also exposed within Harney Peak Granite. Pillow basalt is overlain by ferruginous metachert unit in some parts of Nemo and Pactola Reservoir (PAC) dam. Older Early Proterozoic rocks are overlain by the Younger Early Proterozoic units in the east-central part of the Black Hills region. These rocks consist of conglomerate, debris flow, quartzite, banded iron formation, and alkali basalt. In most of the Black Hills area, Precambrian rocks are overlain by the younger Cambrian Deadwood Formation where it thins out in the southern part of the hills. Deadwood Formation is composed of glauconitic sandstone, shale, limestone, and the discontinuous basal conglomerate (Rich

1981; Strobel et al. 1999). Deadwood Formation is overlain by the Upper Devonian and Lower Mississippian Englewood limestone along the northwestern side of Wind Cave. Mississippian-age Englewood limestone is underlain by Mississippian-age Madison Limestone. Madison Limestone consists of reddish brown sandstone and massive limestone with upper portion mark by karst topography (Rich 1981; Strobel et al. 1999). Due to regional disconformity along the underlain Formations, the thickness of Madison Limestone increases from almost zero in the south to 305 meter (m) in the north (Rahn 1985). The Madison Limestone is unconformably overlain by the Pennsylvanian and Lower Permian Minnelusa Formation. Thickness of Minnelusa Formation increases from less than 120 m in the north to 350 m in the south. Minnelusa Formation consists of cross-stratified sandstone, limestone, dolomite, and shale (Strobel et al. 1999). The upper part of the Minnelusa Formation consists of breccias formed from gypsum and anhydrite (Braddock 1963). Jurassic age Morrison Formation, Unkpapa Sandstone, Sundance Formation, and Gypsum Spring Formation consist of sandstone, siltstone, shale, claystone, and Limestone. Morrison Formation and Unkpapa Sandstone increase in thickness along the eastern side of the Black Hills.

The Inyan Kara Group consists of Lower Cretaceous age sandstone of Lakota and Fall River Formations which form a major hogback surrounded Black Hills. For the southern Black Hills, commercial grade U was produced from the Inyan Kara Group (Webb et al. 1995) composed of sandstone, siltstone, and shale of marine and non-marine units of Lower Cretaceous age. Lakota Formation is overlain by Fall River Formation, and unconformably overlies the Morrison Formation. Lakota Formation is composed of cross-bedded channel-fill sandstone, shale, and limestone having maximum of 152 m, while the Fall River Formation consists of well bedded, fine-grained sandstone, with some siltstone and claystone with maximum thickness of about 61 m (Rich 1981). Outside the hogback, the trace deposits of sand and gravel cover the bottom of the stream valleys at different elevations.

The climate of Black Hills region consists of four seasons, with cold winters and hot summers. The precipitation is relatively low, with the average annual precipitation between 1971 and 2000 in the northern and central part of Black Hills ranges between 61 and 68 centimeter (cm), whereas, it is less than 43 cm in the southern part.

Materials and methods

Sample locations and collection

This study consists of bottom sediments collected from seven reservoirs within the Black Hills region of SD and WY (Fig. 1), including Angostura (ANG), Belle Fourche (Orman) Dam (OD), Deerfield (DF), Keyhole (KR), LAK, Pactola (PAC), and Sheridan (SH). Below are geographic and geologic descriptions for each of the reservoirs, while specific sampling location is provided in Fig. 2.

ANG Reservoir is located on the Cheyenne River, at the southeastern edge of the Black Hills. It was completed in 1949 for irrigation purposes, and has a catchment area of approximately 9100 km^2 from the Cheyenne River of predominantly semi-arid plains across southwest SD, northwest NE, and east-central WY (Green 1990). Rocks of Paleozoic strata, primarily limestone, inter-bedded sandstone and shale are exposed in the northern watershed, while Mesozoic rocks of Fox Hill sandstone, Pierre Shale, Carlile Shale, Greenhorn Limestone, Skull Creek Shale and Inyan Kara Group, Sundance Formation and Spearfish Formation are exposed primarily in the southern edge of the Black Hills. Horsehead Creek is second major source of inflow into the reservoir which mostly drains Pierre Shale and is known source of Se in the region (Green 1990). Samples were collected near the reservoir spillway (ANG 1–1), Cheyenne River inlet (ANG 3–3), and Horsehead Creek Arm (ANG 2–3).

OD Reservoir (906 m elevation) is located at the terminus of Owl Creek, 13 km east of Belle Fourche, SD constructed in 1914 for irrigation purposes. The reservoir periodically collects diversion water from the BF River during high flows. The catchment area is approximately 442 km^2 for Owl Creek and 1664 km^2 above the BF Diversion. The topography of the catchment area is characterized by broad, shallow valleys and gently sloping hills (Roddy et al. 1991). The catchment contains rock exposures from the Hell Creek Formation, Fox Hills Sandstone, Niobrara Formation, Carlile Shale, Greenhorn Limestone, BF and Mowry Shales, and Skull Creek Shale and Inyon Kara Group (Roddy et al. 1991). Samples were collected near the Belle Fourche Reservoir Diversion (OD 2–1) and Owl Creek inlet (OD 1–1).

The DF Reservoir (1802 m elevation) is located 40 km west of Rapid City on Castle Creek. The dam on Castle Creek was constructed in 1947. Deerfield Reservoir has a surface area of 1.68 km^2 and average depth of 9 m. Deerfield Reservoir is nested between two bluffs composed of phyllite and quartz mica schist of Precambrian core in the southeastern portion of the Black Hills. Samples were collected adjacent to the reservoir spillway (DR 1–1), Goldrun Creek inlet (DR 2–1), and Castel Creek Arm (DR 3–1).

KR Reservoir (1258 m elevation) is located within the upper BF River near Moorcroft, WY, USA. Constructed in 1952, the reservoir has a catchment area of 5850 km^2. The catchment lithology is composed of three Cretaceous age geological units, including Lakota sandstone, Fuson shale,

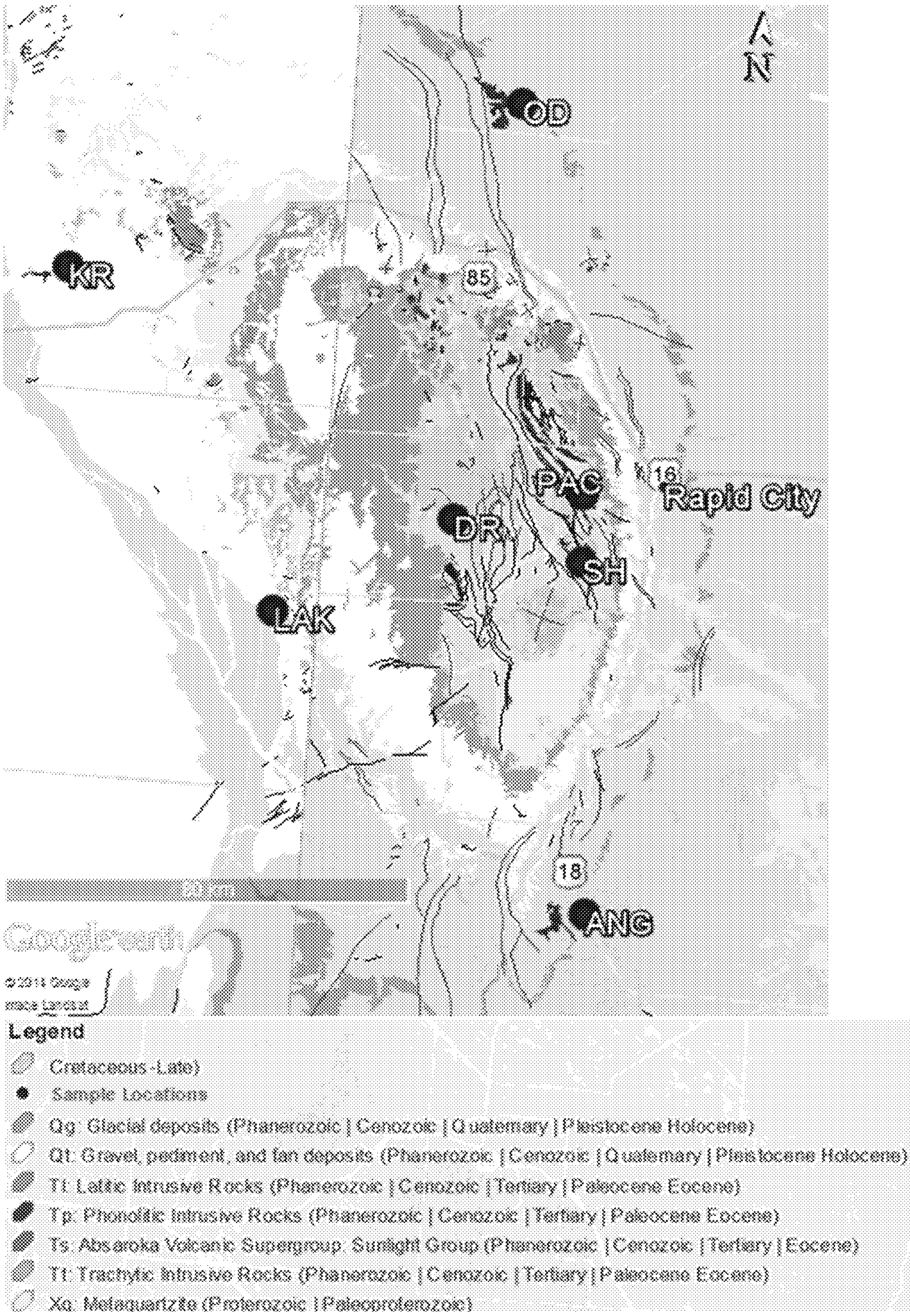


Fig. 1 Locations with Geological map of seven reservoirs: *ANG* angostura, *Orman* Belle Fourche *OD* dam, *DF* deerfield, *KR* keyhole, *PAC* LAK, Pactola, and *SH* Sheridan in the Black Hills region of South Dakota and Wyoming

and Dakota sandstone. Samples were collected at the Eggie Creek Bay (KR 1–1), BF Mull Creek Bay (KR 2–1), and River inlet (KR 3–1).

LAK Reservoir (1335 m elevation) is located on the Stockade Beavercreek on private land, 8 km southeast of Newcastle, WY. The reservoir was constructed in the 1940s. The LAK Reservoir is located on the western edge of the Black Hills in a narrow canyon with steep cliffs. The rocks in the catchment are composed of sandstone and limestone of Minnelusa Formation of Permian age, Minnekahta Limestone and Opeche Shale of Phanerazoic, Paleozoic, and Permian ages and shale, siltstone and gypsum of Spearfish Formation of Paleozoic, Mesozoic age. Samples were collected from the spillway (LAK 1–1).

PAC Reservoir (1388 m elevation) is located on Rapid Creek, 17 km north of Hill City, SD, USA. The dam on the Rapid Creek was constructed in 1956. The normal operating depth at dam is 60.8 m. PAC Reservoir has a surface

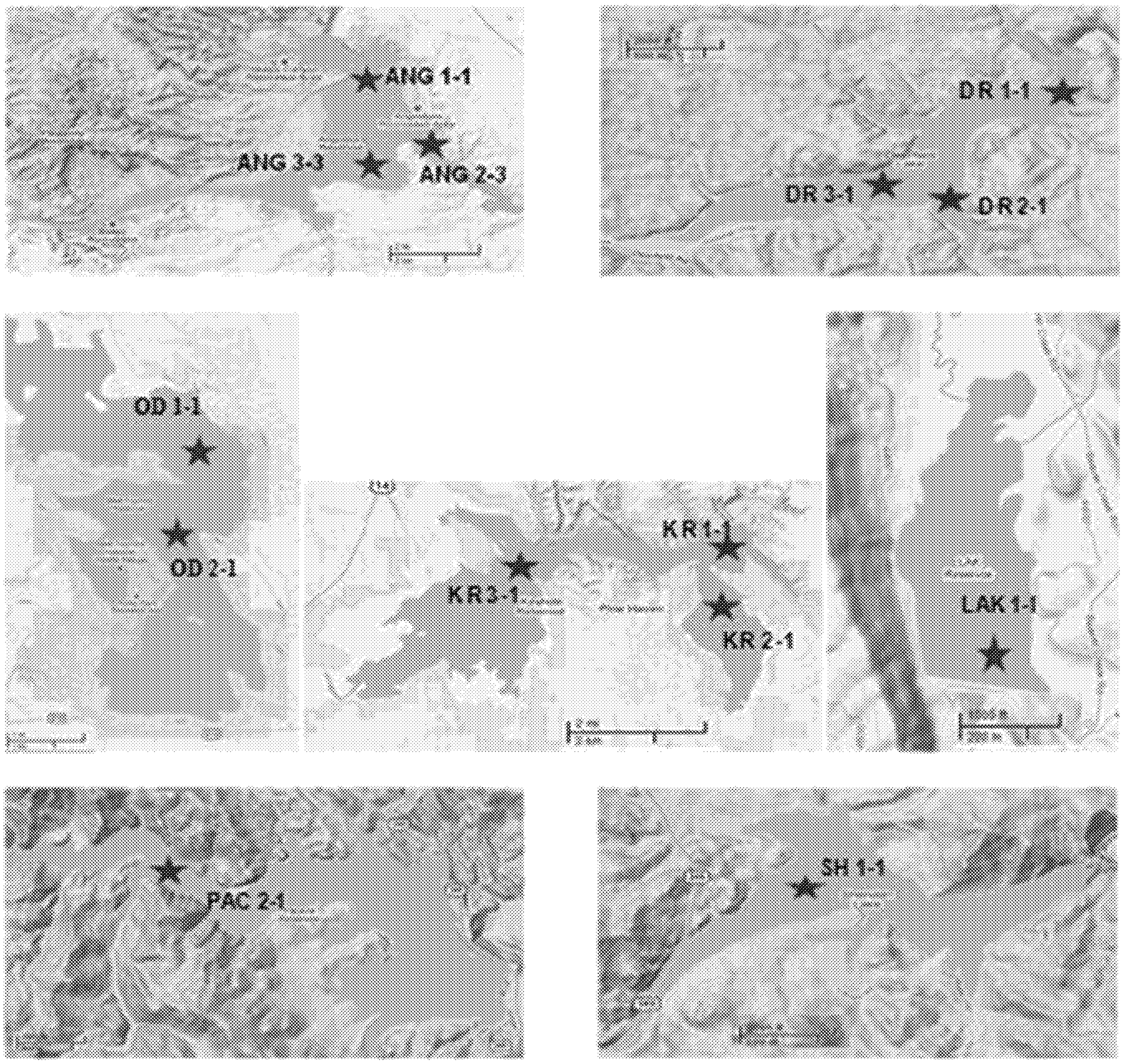


Fig. 2 Sampling location of seven reservoirs: *ANG* angostura, *Orman* Belle Fourche *OD* dam, *DF* deerfield, *KR* keyhole, *PAC* LAK, *PAC* Pactola, and *SH* Sheridan in the Black Hills Region of South Dakota and Wyoming

area of over 5 km^2 at spillway crest level and the catchment area is approximately 86 km^2 for Rapid Creek. Rocks of metamorphosed shale and meta-basalt of Proterozoic age are present in the catchment area of PAC Reservoir watershed. Many small quartz veins and minor pyrrhotite, arsenopyrite, gold mineralization were noted along the Right-Lateral Silver City fault northwest of PAC Reservoir (Redden and DeWitt 2008). One sample was collected from the Rapid Creek inlet (PAC 2–1).

SH Lake (1409 m elevation) is located on the Spring Creek, 9 km northeast of Hill City, SD. The dam on Spring Creek was constructed in the 1930s. Sheridan Lake is located 6 miles south of PAC Reservoir. Spring creek drains approximately 101 km^2 above Sheridan Lake. The geology of the catchments of both SH and PAC is similar due to their close proximity. Sheridan Lake catchment has exposed Alluvium rocks of Phonerozoic, Cenazoic, and Quaternary ages that have clay to bolder size clasts with some organic matter which are absent in PAC Reservoir catchment area. One sample was collected from the Spring Creek inlet (SH 1–1).

Fourteen bottom reservoir sediments were collected from seven reservoirs in the Black Hills region in January and February 2011, with selection based upon previous uranium mining locations and effected watershed locations.

Sediment cores were generally collected from the channel inflow and outflow, and the deepest parts of the reservoirs where the sediment rate was higher and sediments were considered undisturbed from wind. To collect core samples, separate 20 cm diameter holes were drilled into the ice using a gas-powered auger. Water depths were determined using sonar depth locator. One water sample was collected from a separate drill site using 500 mL surface water grab sample (Wildco bomb sampler, Wildlife Supply Company, Yulee, FL) to minimize consolidation of local sediments. Water sample was collected 30 cm above reservoir bed from each sediment core location prior to sampling. After collecting each sample, water-quality parameters were noted including dissolved oxygen (DO), temperature, pH, and conductivity. Two sediment cores were collected from each location (from separate sampling sites) using a 122 cm length suction coring device (Wildco 2400-B20 KB), with cores collected within internal 4.31 cm diameter plexiglass tube. Core samples were sliced into 2–3 cm segments and placed in a 120 mL whirl–pak bags within 24 h of collection, and stored at 0 °C prior to analysis.

Laboratory analysis

One mm diameter pellets were prepared with 0.9 mm of sample powder mixed with 0.1 mm of ultra-bind. Pressed powder pellets were prepared for all fourteen core samples and were analyzed for major and trace elements (Ag, As, Ca, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Rb, SiO_2, Sr, Ti, U, V, and Z) using a Bruker Tracer III-SD hand-held X-ray fluorescence spectrometry (XRF) instrument. Organic matter content was determined by Loss on Ignition (LOI) method following Heiri et al. (2001) procedures:

$$\mathrm{LOI} = 100 \times (\text{Mass loss})/(\text{Sample weight prior to firing}) \quad (1)$$

All 11 water samples were analyzed for total metal analysis (Ag, Al, As, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Rb, Se, Sr, Th, U, V, and Zn) following EPA 200.7 and 200.8 methods.

Statistical methods

Inter-core element correlations were determined using Pearson correlation r representing statistical relationship between two elements (SigmaPlot, Systat Software, San Jose, CA, USA). Values approaching +1 indicate a strong positive correlation, while values approaching −1 indicate a strong negative correlation. Significance of 95 % confidence interval and approach +1 or −1 was assumed for p values <0.04.

Results

Reservoir sediment metal concentrations

While an increase in reservoir heavy metal concentration may be considered an indicator of anthropogenic pollution, metal loading may also be introduced by geologic weathering processes within the catchment. Down-core pattern of chemical concentrations of reservoir sediments is considered helpful in understanding the distribution of elements in samples collected from different reservoir locations. For this study, locations were chosen to investigate contributions in metal concentration emanating via stream flows through diverse geologic sequences. To clarify the elemental downcore pattern elemental concentration data including LOI, five major elements (Ca, Fe, Mn, SiO_2, and Ti), twelve trace elements (Ag, As, Cr, Cu, Mo, Ni, Pb, Rb, Sr, U, V, and Zn), and Rb/Sr ratio were graphed as a function of depth for all Black Hills sampling locations (Figs. 2, 3 ESM).

Reservoir sediment LOI was highest (2.71–20.69 %) at the surface and variable between cores. LOI concentrations in the bottom sediment cores ranged between 1.19 and 29.47 %. The wide range of LOI in the sediment samples suggests that differing source materials were present within the reservoir watersheds. Samples collected from PAC and SH had the highest LOI concentration. PAC and SH also had the highest concentrations of As, Fe, Mn, Ni, Pb, Ti, and Zn. The concentrations of As and Cr were higher in shallow depths compared to the deeper sediments collected from PAC. Both PAC and SH watersheds have a long history of mining activities.

Silica-rich sand with low LOI, Cu, Fe, Mn, Rb, Ti, U, and Zn was present within the Horsehead Creek Arm and the Cheyenne River inlet samples collected within ANG Reservoir. These silica-rich sands ranged from fine to coarse grained and were present at the bottom of the sample cores. The Cheyenne River inlet results were generally lower values compared to spillway samples. The mineralogy of the spillway sediments might be influenced by the streams that drain from the north into ANG reservoir.

Iron and Mn exhibited strong inter-core relation for all samples except those collected near the spillway of ANG and DF Reservoir, and Spring Creek from SL. Iron and Mn generally exhibit similar redox geochemical behavior (Singh and Nayak 2009). Rb/Sr trends may describe weathering intensity within the catchment because mineralization of Rb and Sr shows different preferences depending upon their mineral structure (Xu et al. 2010; Zhangdong et al. 2001). During weak chemical weathering, Rb tends to stay behind, resulting in Rb formation

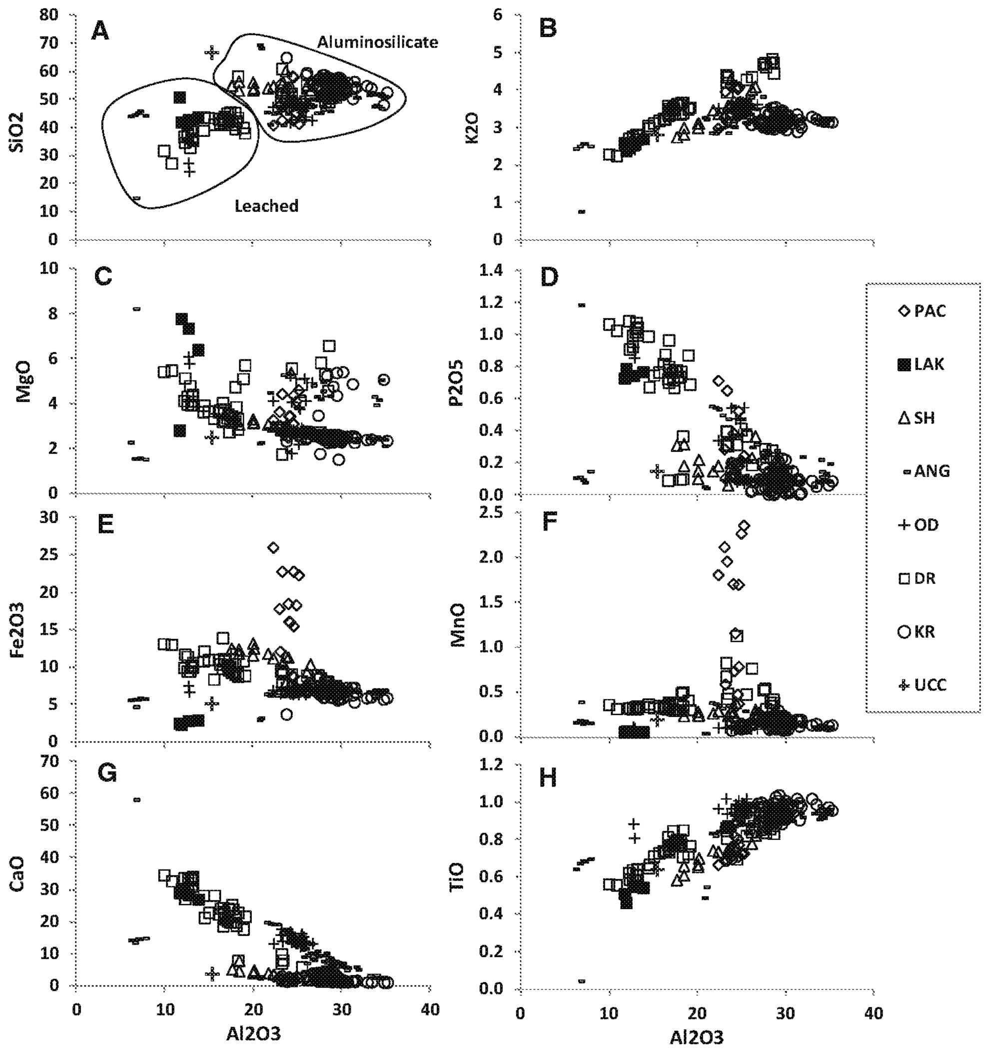


Fig. 3 Chemical variation diagrams for **a** SiO_2, **b** K_2O, **c** MgO, **d** P_2O_5, **e** Fe_2O_3, **f** MnO, **g** CaO, and **h** TiO_2 compared to Al_2O_3 of reservoir sediments. Upper continental crust (UCC) from Rudnick and Gao (2003)

enrichment. With the exception of the KR Reservoir and BF River arm, all samples had elevated Rb/Sr values at depth, suggesting weak chemical weathering of these sediments within these watersheds (Xu et al. 2010; Zhangdong et al. 2001). Strontium and Ca also exhibit similar trends except in samples collected from the spillway in DF Reservoir and SH Lake, and appear attributed to Sr partitioning into Ca-rich minerals (Chen et al. 1999). Calcium peaked at 20 cm depth (7.9 ppm) in SH Lake, while the spillway in DF Reservoir Ca peaked at 5 cm depth whereas Sr remained consistent. The elevated sediment Ca may be attributed to the precipitation of carbonate with low Sr distribution coefficients (Singer and Navrot 1973). Silver, Mo, Pb and U trends were similar for all samples, with U intermittently elevated. For LAK reservoir, there were no significant trends primarily due to low core recovery.

Reservoir sediment spatial distribution

Average compositions of all reservoir sediments are presented in Table 1. Bottom sediments from PAC reservoir and SH Lake were markedly enriched in Mn, Cu, Cr, V, Fe, As, and Rb/Sr ratios. High Fe and As in PAC Reservoir and SH Lake sediments correlated with high pyrrhotite, arsenopyrite in Precambrian rocks of catchment area. The OD sediment samples contained elevated U as compared to other reservoir sediment samples, and appear correlated with major U deposits contained within sandstones and from Inyan Kara Formation of the Powder River basin. Sediment samples from DF and LAK Reservoirs were distinctly enriched in Ca, which may be associated with the limestone of Minnelusa Formation of Permian age. LAK Reservoir contained the lowest metal concentrations for the Black Hills region. LAK Reservoir drains the western part

Table 1 Average sediment compositions from the seven reservoirs in ppm

	ANG	DF	KH	OD	SH	PAC	LAK
Catchment area (km^2)	9100	33	5850	2106	101	86	152
Geology	Paleozoic Ls, Ss, and Sh	Precambrian Phy and Sch	Cretaceous Ss and Sh	Cretaceous Ss and Sh	Alluvium	Proterozoic meta Sh	Permian Ss and Ls
Si02	444,431	710,633	923,451	781,513	526,800	609,692	519,000
Ca	49,018	113,741	14,078	90,527	19,323	15,978	156,500
Ti	3213	2568	4041	3323	2834	3858	1350
V	124	163	115	124	183	287	152
Cr	77	104	88	86	137	356	27
Mn	562	**1455**	665	307	**1137**	**6921**	124
Fe	24,210	**31,659**	26,106	23,530	**38,680**	**62,223**	**7330**
Ni	13	13	12	16	13	33	12
Cu	37	52	36	40	56	63	24
Zn	71	62	72	69	89	181	18
As	7	6	7	10	**86**	**85**	7
Sr	244	108	148	338	98	95	165
Mo	67	81	61	87	71	84	49
Ag	20	33	19	31	27	26	13
Pb	24	34	21	34	34	40	18
U	45	46	41	**60**	41	49	**9**
Rb	96	90	101	102	96	95	37
Rb/Sr	0.46	0.84	0.70	0.35	**0.99**	**1.01**	0.23

Values in bold represent elevated concentration

Ls limestone, *Ss* sandstone, *Sh* shale, *Phy* phylite, *Sch* schist

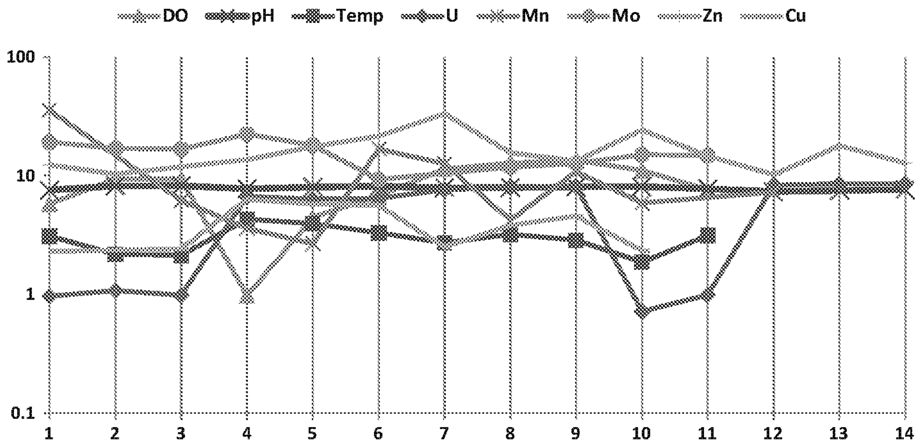
of the Black Hills and is a relatively smaller catchment compared to others from this study.

Elemental concentrations relative to Al_2O_3 are present in Fig. 3. Changes in Ca and organic matter can be evaluated using elemental concentration normalized with Al. It is suggested that the concentration of Al in sediments does not change over 10,000 years (Bertine and Goldberg 1977). Higher ratio of SiO_2/Al_2O_3 is noted in shallow sediments from the samples collected near the spillway in ANG Reservoir, LAK Reservoir, and SH Lake and bottom sediment sample collected from the Cheyenne River arm in ANG Reservoir. Higher ratio of SiO_2/Al_2O_3 ratios in these sediments is likely due to low Al-rich minerals and feldspar and high quartz. All other reservoir samples had relatively constant SiO_2/Al_2O_3 suggesting dilution of minerals like hematite, calcite, or opaque minerals with little or no SiO_2 and Al_2O_3 (Cullers 2000). Samples collected near spillway and from Cheyenne River arm in ANG Reservoir mostly have low SiO_2/Al_2O_3 ratio relative to other samples. This can be linked to enrichment of Al-rich minerals like Koalinite and Illite relative to quartz in these sediments.

Reservoir water quality

Although trace elements such as As, Pb, Cd, and Cr are minimally present in natural waters, they are very important factor in water-quality viewpoint. Results of water samples collected from the water column immediately above the bottom sediments from the reservoirs in the Black Hills region are presented in Fig. 4. If the pH of an aqueous solution is known, the stability of minerals in contact with the water may be determined. For example, Cu, Ni, Hg, and Ca are highly stable in natural waters and can adversely affect water quality of the reservoirs (Förstner 1976). The pH of water samples ranged from 7.35 collected near spillway of ANG to 8.2 from the Castel Creek arm in Deerfield Reservoirs. The water sample collected near spillway in Keyhole Reservoir has the lowest DO concentration, and could be due to the number of factors such as lack of inflowing water, temperature, and extensive ice cover (Guenther and Hubert 1991). Uranium concentrations were all below the mean contaminant levels (MCL) of 30 μg/L (EPA 2011). Arsenic (8.89 μg/L) was only detected in SH Lake, while Fe, Ni, and Th were not detected in any lakes.

Fig. 4 Dissolve oxygen (mg/L), pH, temperature (°C) and concentrations of U, Mn, Mo, Zn, and Cu (μg/L) for water samples collected. *1* DR 1, *2* DR 2, *3* DR 3, *4* KR 1, *5* KR 2, *6* KR 3, *7* LAK 1, *8* OD 1, *9* OD 2, *10* PAC 2, *11* SH 1, *12* ANG 1, *13* ANG 2, *14* ANG 3



Discussion

Major elements

Major oxide values are used to classify the rock types and construction of chemical variation diagrams, with the latter commonly used to present the relationship between elemental data and geochemical processes. In Fig. 3, Al_2O_3 shows the most chemical variation among all oxides ranging from 5.9 to 35.2 wt%. Due to Al high abundance and its relatively small inputs from anthropogenic source, it was plotted on the horizontal axis vs other major oxides on the vertical axis, and compared to reservoir sediments and the estimated averages of the upper continental crust (UCC) (Rudnick and Gao 2003). Al_2O_3 in sediments increased towards finer grain (clay) and SiO_2 increases towards coarse grains (sand) (Das and Haake 2003; Vital and Stattegger 2000). Similarly, other elements that exhibited similar behavior are Fe_2O_3, TiO_2, MgO, and K_2O. If sediment has grain size effects from sand to mud, it shows smooth trends. Variation diagrams of major oxides of present study show that Fe_2O_3 and MgO did not indicate smooth trends againstBlack Hills sampling locations Al_2O_3, while SiO_2 and Al_2O_3 show differing patterns which suggest that there was no grain size effect from sand to mud in these sediments. In mud, CaO is negatively correlated with Al_2O_3 (Vital and Stattegger 2000). The results suggest that samples collected from reservoirs of Black Hills region consist primarily of clay minerals.

Inter-core element correlations were determined using Pearson correlations (Table 2 ESM). With the exception of LAK, U generally had strong correlations with Mo (0.805–0.954), Ag (0.477–0.882), and Pb (0.642–0.889) in all reservoirs. The strong negative correlation of Rb/Sr to Ca (−0.928 and −0.851) and strong positive correlation of Rb/Sr to Rb (0.748 and 0.917) in ANG and OD sediments, respectively, indicate chemical weathering and sorting. Further, the correlation between SiO_2 and Rb (0.528) determined within OD sediments suggests chemical weathering in the catchment area. Strong correlation of As to Fe (0.787) in PAC Reservoir and 0.805 in SH Lake suggests the presence of similar mineral phase such as arsenopyrite. Positive correlation of Zn to Ti (0.451–0.695) and Fe (0.467–0.911) in ANG, OD, and KR sediment samples indicates the presence of Ilmenite group of minerals. Similarly, strong positive correlation of Sr to Ca (0.880–0.982) in ANG, OD, and KR sediment samples suggests calcite mineral phase controls and potential of chemical weathering. For SH Lake, a strong negative correlation of Fe to Mn of −0.612 suggests that differing geological sources may exist in the catchment (Larson and Stone 2011). Vice-a-versa, a strong positive correlation of Fe to Mn of 0.808 and 0.694 in PAC and Keyhole Reservoirs, respectively, indicates similar source or post-depositional behaviors (Singh and Nayak 2009).

The Fe_2O_3 and MnO to Al_2O_3 comparisons (Fig. 3e) from PAC suggest that excess Fe_2O_3 and MnO were present, and could be attributed to enrichment of biotite and ferromagnesium minerals. In addition, there appears to be contribution from high arsenopyrite in Precambrian rocks common within the PAC catchment (Table 1). LAK, DF, and sediment at depths of 18–22 cm from BF inlet of OD Reservoir samples contained relatively low SiO_2 and Al_2O_3, and high CaO. These sediments also had relatively high Ca and MgO. This is consistent with the calcite and Mg found within the Minnelusa Formation and calcite in Minnekahta Limestone common to these catchment areas. Variation diagrams in Fig. 3 indicate that, as Al_2O_3 increased, TiO_2 and K_2O increased, whereas P_2O_5 and CaO decreased. MnO, Fe_2O_3, SiO_2, and MgO remained consistent, while the linear trends of TiO_2 and K_2O against Al_2O_3 appear attributed to the presence of clay minerals. P_2O_5 and CaO showed negative trends against Al_2O_3, which may be attributed to the presence of minerals like apatite and epidote and depletion of detrital clay minerals in LAK and some OD 2–1 samples. The major oxide concentrations of reservoir sediments of Black Hills region were generally higher compared to UCC. This could be due to the loss during sedimentary processes and strong physical weathering of rocks in the catchment area (Borges et al. 2008). For the SiO_2 vs Al_2O_3 comparisons (Fig. 3a), most samples were depleted in SiO_2 compared to UCC indicating the presence of carbonate minerals. Al_2O_3 in reservoir sediments indicates two differing trends when compared to UCC. LAK, sample collected near spillway from DR, and select sediments from BF River inlet, and near spillway and Horsehead Creek inlet from ANG were depleted in Al_2O_3 compared to UCC, suggesting the loss of Al-rich clay minerals and feldspar (Borges et al. 2008; Cullers 2000).

The major elements determined in the reservoir sediments reflect the type of rocks in the catchment area. Fe_2O_3/K_2O vs SiO_2/Al_2O_3 ratio (Herron 1988) diagrams are commonly used to describe the sedimentary rocks, which present index of chemical maturity and measures mineral stability in the sediment. Herron's classification diagram has been successfully applied to the modern unconsolidated sediments (Vital and Stattegger 2000). The diagram scheme from Herron (1988) has been applied to the reservoir sediments from Black Hills region (Fig. 5a). Sediments at depths of 0–10 cm collected from Horsehead Creek arm of ANG Reservoir and 2–4 cm from LAK Reservoir may be classified as litharenite and wacke, respectively. Herron diagram is effective in distinguishing Fe-rich PAC, SH, and DF Reservoirs sediments. The Black Hills reservoir sediments generally lie within the shale range which is consistent with black shale common to the region. Sediments collected from LAK Reservoir have comparatively higher CaO than sediments collected from the other reservoirs (Fig. 5b), which is consistent with the calcite found within the Minnelusa Formation and Minnekahta limestone common to that catchment. All other reservoir sediments were generally consistent with the Pierre Shale and UCC.

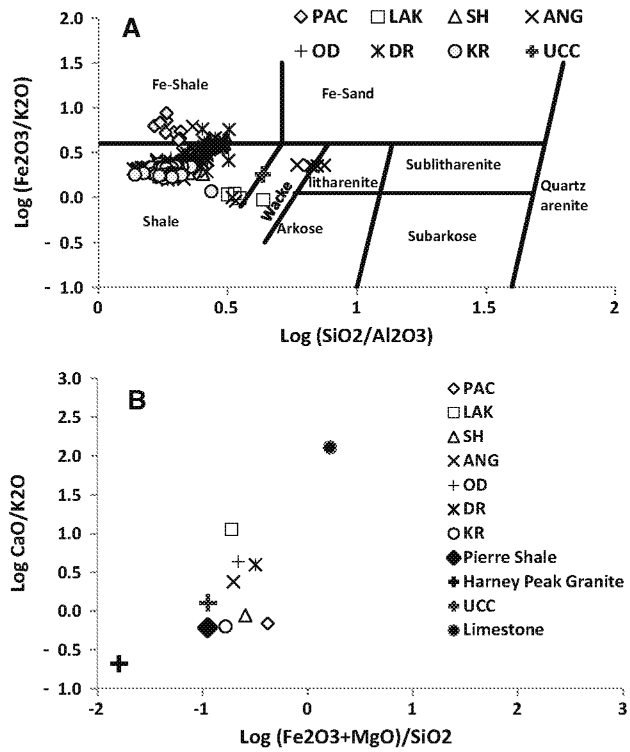


Fig. 5 **a** Chemical maturity and measures mineral stability (Herron 1988), and **b** geochemical view of origin of sediments in the reservoir sediments (Railsback 1993). Geochemistry of Harney Peak granite from (Duke et al. 1992). Data sources for Upper continental crust (UCC) (Rudnick and Gao 2003), Pierre Shale (Tourtelot 1962), limestone (Clarke and Washington 1924)

Minor elements

Trace element ratios may be more informative than concentration when comparing reservoir sediments with catchment geology. Clay-rich sediments generally have higher concentration of trace elements resulting from the influence of provenance, weathering, and grain size sorting. For this reason, many reservoir sediment studies have successfully utilized clay and heavy metal profiles for provenance determination (Vital et al. 1999; Vital and Stattegger 2000). This is especially true since high-field strength elements (HFSE) such as Zr, Hf, Ti, Pb, and U, and transition elements such as Cr, Mn, Fe, Ni, Cu, and Zn are relatively immobile and exhibit low solubility. Their low solubility attributes suggest that they may be transported as suspended particles and, therefore, the geochemistry of the source rock remains present. For example, immobile La and Th are more abundant in felsic rocks, while Sc and Co are more abundant in basic rocks (Nyakairu and Koeberl 2002). Large ion lithosphere elements (LILE) such as Rb and Sr, while typically fluid mobile, are subject to weathering. The average sediment values for our study are presented on UCC-normalized spider diagrams in Fig. 6. With the exception of PAC and LAK Reservoirs, spider diagrams show anomalies within Cu, Sr, Zr, Hf, Ti, Pb, and U for all samples. All samples were more enriched in HFSE and strongly depleted in Ni. Chromium, Mn, Fe, and Sr were depleted in most samples. HFSE shows similar patterns for all samples, except for LAK Reservoir which had relatively slightly low abundance of Ti and U, consistent with the limestone of Minnelusa Formation of that catchment. Zr, Hf, and U were associated with heavy elements which are resistant to the weathering like zircon. All samples demonstrated enrichment of Zr, Hf, and U compared to the UCC. Enrichment of U in particular suggests

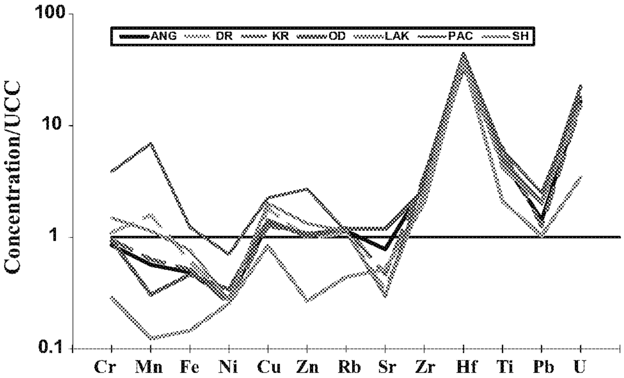


Fig. 6 Upper continent crust normalized spider diagram of reservoir sediments

weak chemical weathering (Singh and Nayak 2009), while enrichment of Hf and Zr could be due to the presence of zircon in the source rock.

The negative correlation between Sr and Rb/Sr suggests chemical weathering in the catchment area of the ANG Reservoir (Fig. 7a). In similar fashion, the shallow depth sediments collected near spillway from ANG Reservoir had low Rb/Sr ratio and higher Sr concentration compared to UCC, suggesting strong chemical weathering within the catchment area. However, the bottom sediments collected near spillway from ANG Reservoir had high Rb/Sr ratio and low Sr concentration compared to UCC, suggesting strong physical weathering in the catchment area. These differences may be attributed to seasonal variations such as

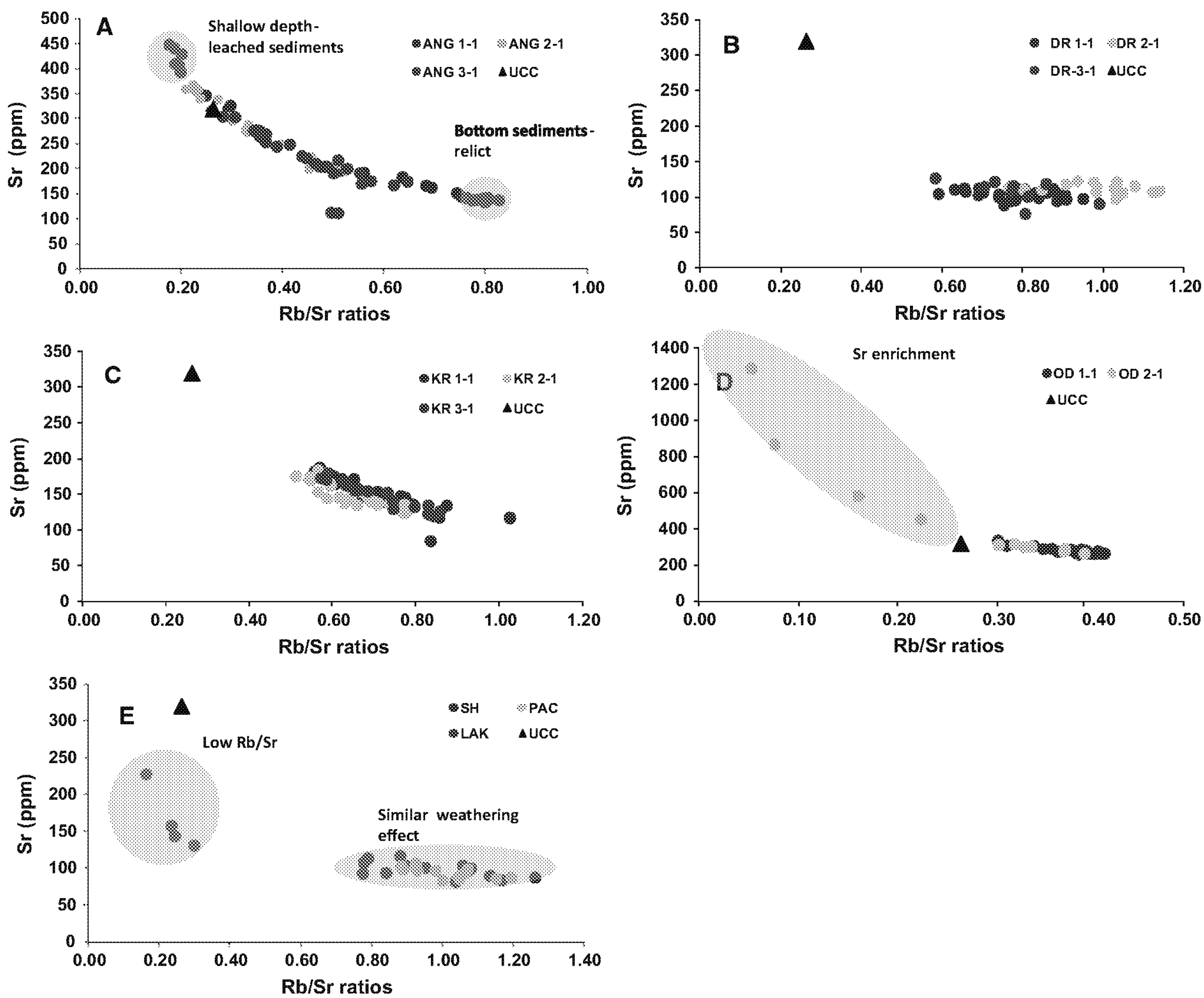


Fig. 7 Rb/Sr ratio of the reservoir sediments at **a** ANG, **b** DR, **c** KR, **d** OD, **e** SH, PAC and LAK compared to UCC. UCC from (Rudnick and Gao 2003). *Gray* shading indicates weathering effects

transport of coarse sediments as bed load from rapid snowmelt and/or flooding, and fine sediments reflect suspended transport resulted in summer rainfall.

Sediment sample collected from BF inlet of OD Reservoir had lower Rb/Sr ratio and high Sr of bottom sediment suggesting strong chemical weathering of these sediments (Fig. 7d), while the Owl Creek arm of OD Reservoir shows weak chemical weathering. KR Reservoir sediments have intermediate to low Sr and high Rb/Sr ratio compared to the UCC, and exhibited a negative correlation with Rb/Sr ratio suggesting combination of both physical and chemical weathering in catchment area (Fig. 7c). DF Reservoir sediments had low Sr and high Rb/Sr ratio compared to UCC (Fig. 7b), while there was no change in Sr as Rb/Sr ratio increased suggesting strong physical weathering in catchment area of DF Reservoir. The negative correlation between Rb and Rb/Sr suggests strong physical weathering in the catchment area of PAC Reservoir and SH Lake (Fig. 7e), while LAK Reservoir had low Rb and Rb/Sr ratio suggesting that chemical weathering processes were dominant.

Conclusion

The reservoir sediment metal results show that Ag, Mo, Pb and U generally exhibit similar trends across all Black Hills region reservoirs. PAC Reservoir and SH Lake had the highest As, Fe, Mn, and Rb/Sr ratios. OD Reservoir had the highest U concentration compared to all other reservoirs, while LAK Reservoir generally had the lowest metal concentrations. With the exception of ANG and LAK Reservoirs, all Black Hills reservoirs appear dominated by physical weathering processes from within their respected watersheds, while all reservoir samples except LAK that exhibited higher HFSE compared to UCC. HFSE are considered relatively immobile and least soluble trace elements suggesting that physical transport via suspended particulates may be the dominant transport mode. These trends are consistent with the detrital component of the sediments transported from the source areas. The anthropogenic activities such as historic gold mining in the north and central Black Hills, and U mining in the southern Black Hills may contribute to the physical transport of contaminant loading to the reservoirs; however, the relative magnitude of contaminants determined within the sediments is minor. Aqueous U was consistently below the drinking water mean contaminant levels (MCL) of 30 μg/L (EPA 2011), while As (8.89 μg/L) was only detected within SH Lake. Results suggest that the reservoir sediments and waters sampled from the Black Hills region appear largely unaffected by the abandoned mines located within the reservoir catchments.

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